Journal of Thermal Analysis, Vol. 47 (1996) 1759-1762

ON THE PYROLYTIC DECOMPOSITION OF CADMIUM CARBONATE
Thermogravimetry and exoemission of electrons

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(Received March 5, 1995; in revised form January 20, 1996)

Abstract

The pyrolytic decomposition of cadmium carbonate was studied by thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermoanalysis (DTA) and exoemission of electrons (EEE).

Keywords: cadmium carbonate, cadmium oxide, derivative thermogravimetry, differential thermal analysis, Gibbs energy, phase change

Introduction

The phenomenon of pyrolytic decomposition of cadmium carbonate $CdCO_3$ has been intensively studied for many years [1–6]. Cadmium carbonate decomposes under atmospheric pressure at a temperature of 580 K. The decomposition yields CdO without the formation of intermediates:

$$CdCO_3 \rightarrow CdO + CO_2$$

The method of exoemission of electrons is widely applied to study the phase transformation of various materials, but it has not been applied to investigate the decomposition of cadmium carbonate. The exoemission electrons (EEE) is a non-stationary emission of low energy particles (mainly electrons, sometimes positively charged particles and even neutral particles) from thermodynamically unstable systems during their returning to the equilibrium state. The ejection of electrons from a specimen by external perturbations (e.g. irradiation, quenching or mechanical deformation) is commonly named excitation. It is necessary to supply the additional energy in order to induce emission of electrons. The additional portion of energy is called stimulation. The most common stimulation proceeds by illumination (photostimulation with light of appropriate wavelength

0368–4466/96/ $ 5.00

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limit, energetically below the external photoeffect) during the heating or cooling of the materials studied. In the experiments the temperature is usually raised linearly as a function of time.

Johannes Kramer was the first to investigate the phenomenon of EEE. He published his first papers on the subjects in the early fifties [7–8]. Since then, the phenomenon of exoelectron emission has been widely investigated.

The phenomenon of EEE is often used in studying surface states, defect structures, in dosimetry and postradiation effects, breaking of bonds in the solid state, electron hopping and so on. It has been shown that the technique of EEE can be used in the investigation of the thermal decomposition of some silver salts [10] and superionic conductors [11]. The exoemission of electrons (EEE), along with other material characteristics, is applied to study materials especially during phase changes of the first and second order. It has been shown in a previous paper that the catalytic activity of a chemical reagent is bound to activity centres where electron exchange is easy to occur [12]. It is a significant feature of materials when we try to understand the emission of electrons from catalysts.

Experimental conditions

Thermoanalytical measurements were carried out on a Mettler TA1 Thermoanalyser, at a constant heating rate of 10°C min^{-1}, using PtIr crucibles and Pt–PtRh110 thermocouples. The reference material was α–Al_2O_3 and the sample mass 200 mg.

The temperature dependence of photostimulated exoemission of electrons (EEE) was measured with an air point counter described by Stepniowski [9]. The measurement set-up applied in this work has been described earlier [13]. As a quenching mixture saturated ethanol was used over the surface of its liquid in air as environment. The counter and the ethanol were kept at a constant temperature of 317.5 K using a Hoeppler's thermostat. The carbonate sample was spread in a layer of 1 mm thickness on a steel core which served as a crucible. The core was situated inside the heater. A Fe–Constantan thermocouple was placed just under the surface of the holder (0.5 mm beneath). Between the examined carbonate sample and the counter the accelerating voltage was 100 V cm^{-1}. The samples were illuminated with an unfiltered UV radiation from a quartz lamp with a Q-400 burner. The carbonate samples had not been subjected previously to any of the following effects: radiation, deformation or thermal quasi-stable decomposition. All the tested samples were heated during the experiments at the same constant rate of 10°C min^{-1}. The examined cadmium carbonate $CdCO_3$ was of analytical grade produced by POCH Gliwice – Poland. The thermoanalytical and electron emission measurements were carried out under atmospheric pressure.

Results and discussion

As it is shown in Fig. 1, the decomposition of cadmium carbonate begins at 507 K (mass loss up to this temperature: 0.7%). The total mass loss is 27.15% and the decomposition process at about 807 K. It should be noted that a 0.7% change in mass is regarded as the limit for estimating the level of the beginning and end of a process.

The DTG curve shows a sharp minimum at 718 K. In the applied range the reaction is the fastest at this temperature. The DTA curve corresponds to the DTG curve. In Fig. 1 we can also see an increase in the intensity of exoelectron emission of electrons at $T > 500$ K. The maximum of EEE is at 840 K. It reflects the dynamic behaviour of the changing phases.

During the decomposition process few phenomena occur: a phase change in the solid, evolution of a gas and related phenomena. The phase change in the solid is a transformation of the calcite lattice of $CdCO_3$ to CdO of NaCl-type. The evolved gas consists of CO_2 molecules. According to data given in [14], the

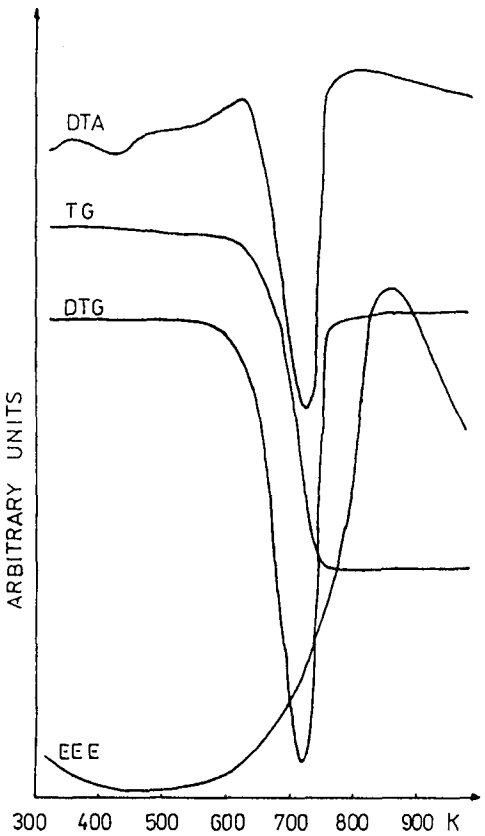

Fig. 1 TG, DTG and DTA curves and EEE intensity *vs.* temperature of $CdCO_3$

Gibbs' free energy is zero at 590 K. It comes from the short consideration as follows:

$$\Delta G = \Delta H - T\Delta S$$

$$\text{If } \Delta G = 0, \text{ then } T = \frac{\Delta H}{\Delta S} \approx 590 \text{ K}$$

The phase change mentioned above needs energy to break one of the C–O bonds (of the three in the molecule of $CdCO_3$).

The temperature at which the Gibbs' free energy is zero should be regarded as the thermodynamic temperature of the decomposition reaction which proceeds in a reversible manner. As calculated above, the temperature of the reversible reaction of cadmium carbonate is 590 K.

However, during our experiments the decomposition proceeded in an irreversible manner.

The thermal decomposition of manganese carbonate is similar, but it is more complicated because of the various oxidation states of manganese. Studies on the carbonates of manganese and other metals are in progress.

References

1 D. W. N. Ivanova, Tiermogrammy minerallov, Zapiski Vsesojuznogo Mineralnogo Obscestva, Leningrad 1961.
2 L. G. Berg, Vvedenije v termografiju, Nauka, Moscow 1969.
3 W. W. Wendlandt, Thermal Methods of Analysis, Wiley and Sons Inc., New York, London, Sydney, Toronto 1974.
4 D. Schultze, Differential Thermoanalyse, VEB Deutscher Verlag der Wissenschaften, Berlin 1969.
5 K. H. Stern and E. L. Weise, High Temperature Properties and Decomposition of Inorganic Salts, Part 2 Carbonates, NSRDS-NBS 30, National Bureau of Standards U.S., November 1969.
6 G. Liptay, Atlas of Thermodynamical curves, Akadémiai Kiadó, Budapest 1977.
7 J. Kramer, Zs. Phys., 125 (1949) 739.
8 J. Kramer, Der Metallische Zustand, Vandenhoeck-Ruprecht, Getyngen 1950.
9 I. Stepniowski, Acta Phys. Polonica, 30 (1966) 163.
10 T. Górecki, Cz. Górecki and L. Biernacki, Thermochim. Acta, 130 (1988) 329.
11 Cz. Górecki, T. Górecki and L. Biernacki, Solid St. Ionics, 27 (1988) 125.
12 L. Biernacki, Cz. Górecki and T. Górecki, Jap. J. of Appl. Phys., 24 (1986) 116.
13 T. Górecki and B. Sujak, Acta Phys. Polonica A, 42 (1972) 487.
14 I. B. Barin, O. Knacke and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer Verlag, Berlin, Heidelberg, New York 1973 and Supplement 1979.